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ABSTRACT (Maximum 200 words)

The combustion of liquid-propellant spray offers new challenges for optical diagnostics. During the four years of ARO support, we have attempted to apply nonlinear optical spectroscopy as an in-situ probe to the determination of the chemical composition in the droplet and the droplet size.

Droplets of low molarity ammonium nitrate in water are used as test samples. The SRS spectra of such droplets consist of two peaks at the vibrational-shifted frequencies of the nitrate ions and of the water molecules. The frequency shifts of the simulated Raman scattering (SRS) from the input laser frequency are equal to the vibrational frequencies. The dominant SRS peaks associated with the nitrate ions and water molecules are noted to consist of a series of equally spaced peaks which are attributed to morphology-dependent resonances of a droplet. The droplet radius can be accurately deduced from the wavelength spacing of the series of SRS peaks. The SRS intensity ratio of the nitrate peak and the water peak is proportional to the logarithmic ratio of the nitrate concentration and water concentration. The incident laser and SRS intensities inside the droplets are high enough to produce third-order sum frequency generation and two-photon absorption.

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INTRODUCTION

The combustion of liquid-propellant spray (consisting of a water solution of tri-ethanol ammonium nitrate), which has the unique property of possessing self-contained oxidizers, offers new challenges for optical diagnostics capable of providing information about droplets. The present research is directed toward exploring the use of nonlinear optical techniques as in-situ probes of the chemical and physical properties of microparticles.

During the four years of ARO support, significant progress has been made toward furthering the understanding of nonlinear optical effects in single liquid droplets with radius, a , much larger than the input laser wavelength (λ_{input}), i.e., droplets with large size parameters $x = 2\pi a/\lambda_{\text{input}}$. We have attempted to apply nonlinear optical spectroscopy to the determination of the chemical composition of the droplet and the droplet morphology (size, shape, and index of refraction). Our research efforts can be divided into two parts: (1) understanding of nonlinear optical effects; and (2) chemical composition and size determination.

A micrometer-size transparent droplet acts as a thick lens to focus the input radiation just outside the droplet shadow face and to concentrate the input radiation mainly in a region just inside the droplet shadow face. Although the external intensity maximum is an order of magnitude larger than the internal intensity maximum, laser-induced breakdown (LIB) can be initiated within the shadow face of salt-free water droplets with $a < 60 \mu\text{m}$. The addition of salt further lowers the LIB threshold within the salt containing water droplets.

A micrometer-size transparent droplet also acts as an optical cavity to provide feedback (with high Q factor) for the internally generated nonlinear radiation. In addition, a droplet with a large size parameter gives rise to a quantum electrodynamic (QED) effect that

causes the spontaneous emission coefficient to be enhanced. Consequently, at input laser intensities below the LIB threshold, several nonlinear optical processes can occur within the droplets. In particular, stimulated Raman scattering (SRS) and third-order sum frequency generation (TSFG) can be produced in single droplets.

The frequency shifts of the stimulated Raman scattering (SRS) from the input laser frequency are equal to the vibrational frequencies of the polyatomic ions and molecules in the aqueous droplet. Droplets of low molarity ammonium nitrate in water are used as test samples. The SRS spectra of such droplets consist of two peaks at the vibrational-shifted frequencies of the nitrate ions and of the water molecules. The dominant SRS peak associated with the nitrate ions is noted to consist of a series of equally spaced peaks which are attributed to morphology-dependent resonances of a droplet with a fixed radius and the index of refraction of the liquid. The dominant SRS peak associated with the water molecules is also noted to consist of a series of equally spaced peaks. The droplet radius can be accurately deduced from the wavelength spacing of the series of SRS peaks.

The SRS intensity ratio of the nitrate peak and the water peak is proportional to the logarithmic ratio of the nitrate and water concentration. The incident laser and SRS intensities (both in the near infrared) inside the droplets are high enough to produce third-order sum frequency generation in the blue. Furthermore, the internal laser and SRS intensities are high enough to induce two-photon absorption which can limit the SRS intensity and can introduce inaccuracy in the concentration measurement. A theoretical model is being developed which incorporates two-photon absorption effects on the growth of the SRS within the droplet.

RESEARCH ACCOMPLISHMENTS

A brief summary is presented of our main findings related to the fundamentals of nonlinear optical effects in single droplets and to the application of nonlinear spectroscopy to chemical composition and size determination of nitrate and sulfate containing water droplets. Details of our accomplishments can be found in the publications resulting from the research (see page XX).

1. FUNDAMENTAL OF NONLINEAR OPTICAL EFFECTS

(a) Q factor and Decay of Nonlinear Waves

The droplet acts as an optical cavity with high Q factor to provide the necessary feedback for SRS generated within the droplets. In order to correlate the detected SRS intensity with the species concentration, it is essential that the Q factor of the droplet be quantified. Traditionally, the Q factors have only been estimated from the Lorenz-Mie calculations of the morphology-dependent resonances (MDR's). Based on these calculations, the Q factors can exceed 10^{30} , which is unrealistically high. The Q factors have been measured from the linewidths of the MDR-related peaks in the various spectra, such as SRS, lasing, fluorescence, spontaneous Raman scattering, and elastic scattering. With such spectroscopic techniques, the upper limit of the Q factor is set by the spectrometer resolution, which is $\approx 10^5$.

Our Q factor determination is based on the temporal measurement of the radiation leakage time τ of the SRS trapped within the droplet. Because $\tau = Q/\omega_{1s}$, where ω_{1s} is the 1st-order SRS frequency, the larger the Q factor the easier to measure the radiation leakage time of the SRS. The maximum Q factor which we deduced from the time domain technique is 10^7 . This value is undoubtedly limited by the intensity depletion, which is another form of loss that can be added to the expected leakage loss from the droplet surface. In our τ measurement of the SRS, two intensity depletion effects can shorten the

measured τ . First, the input radiation can be depleted in generating the 1st-order Stokes SRS. Second, the 1st-order SRS can be depleted in generating the 2nd-order Stokes SRS. In order to eliminate the latter, the input intensity must be kept low enough so that the intensity of the 1st-order Stokes SRS is below the threshold to generate any 2nd-order Stokes SRS. Intensity depletion of the input radiation is difficult to avoid and, thus, may always contribute to setting an upper limit on the maximum Q factor of the SRS waves circulating within the droplet rim. Publications 1 and 2 provide the specifics of our measurements on the Q factor and decay of SRS in single droplets.

(b) Time Dependence of Multiorder SRS Waves

The input laser generates the 1st-order Stokes SRS waves through the first-order Raman gain process. The internal intensity of the 1st-order Stokes SRS waves can be so intense that it can generate the 2nd-order Stokes SRS waves again through the first-order Raman gain process. Such cascade generation of multiorder Stokes SRS has been observed up to the 20th-order Stokes SRS in CCl_4 droplets. The Raman frequency of the n th-order Stokes SRS is $\omega_{\text{ns}} = \omega_{\text{laser}} - n\omega_{\text{vib}}$, where ω_{vib} is the vibrational frequency of the molecule.

The multiorder SRS from 4 M NH_4NO_3 water droplets is collected and dispersed by a spectrograph. The dispersed spectrum is channeled by a fiber ribbon with one end aligned horizontally at the spectrograph exit plane and the other end vertically at the streak camera entrance slit. The streak camera sweeps the entire slit image across its output phosphor, which is then read by a vidicon camera. A portion of the incident laser beam is channeled by an optical fiber to the top portion of the entrance slit of the streak camera. With this experimental arrangement, we measured simultaneously the time behavior of the laser pulse, the elastic scattering from the droplet, the 1st-order Stokes, and the 2nd-order Stokes SRS. By changing the spectrograph setting, we measured simultaneously the time

behavior of the laser pulse and three orders of Stokes SRS (e.g., 1st- through the 3rd-order Stokes SRS or the 2nd- through the 4th-order Stokes SRS).

The long time delay between the 1st-order Stokes SRS and the input laser pulse is the buildup time of the amplified Raman radiation starting from spontaneous Raman noise at $\omega_{1s} = \omega_{\text{laser}} - 1\omega_{\text{vib}}$. The relatively short time delays between the 1st- and higher-order Stokes SRS is because the higher-order Stokes SRS can start from two "noise" sources. First, as is the case for the 1st-order Stokes SRS, the 2nd-order Stokes SRS starts from spontaneous Raman noise at $\omega_{2s} = \omega_{\text{laser}} - 2\omega_{\text{vib}}$. Second, the the 2nd-order Stokes SRS starts from parametrically generated noise resulting from the four-wave mixing of the three optical fields, $\chi^{(3)}E(\omega_{1s})E(\omega_{1s})E^*(\omega_{\text{laser}})$, where $\chi^{(3)}$ is the 3rd-order nonlinear susceptibility. The short time delay between the 2nd- and 1st-order Stokes SRS implies that the parametric noise is initially larger than the spontaneous Raman noise and that the the amplification of the 2nd-order Stokes SRS starts mainly from the parametric noise. Similarly, the short time delay between the $(n + 1)$ th- and n th-order Stokes SRS is because the parametrically produced noise is larger than the spontaneously produced noise. Publication 3 provides the specifics of our results on the growth of multiorder Stokes SRS waves.

(c) Plasma Quenching of SRS Waves

Because LIB threshold is low in high molarity NH_4NO_3 water droplets, we investigated the quenching of the SRS because of the plasma produced by LIB in 4 M NaCl water droplets. The LIB generated plasma can cause enough optical absorption and scattering to totally quench the SRS within a water droplet. LIB is initiated within the shadow face region and during the rising portion of the input pulse, for input laser intensity above the LIB threshold of salt containing water droplets. The resultant plasma within the shadow face region absorbs the remaining portion of the input pulse. A plasma wave or a laser-supported detonation wave is generated and travels from the shadow face toward the

illuminated face. The LIB generated plasma also absorbs and scatters the internal SRS each time the SRS waves traverse the localized region in which LIB is initiated.

Our temporally resolved results indicate that SRS of H₂O vibration (O-H stretch mode) is quenched by the plasma before we can detect the plasma emission from the atomic species (such as Na and H) within the plasma. At very high input laser intensity, LIB is initiated and plasma emission is detected without detectable amount of SRS. At such high input intensities, the plasma absorption and scattering completely prevent the buildup of SRS. Consequently, LIB process sets an upper limit on the input intensity that can be used to generate SRS from nitrate containing water droplets. Publication 4 provides the specifics of our results on the quenching of the SRS by LIB generated plasma.

(d) Third-Order Sum Frequency Generation

The 1st-order Stokes SRS can be so intense that it generates the 2nd-order Stokes SRS in single droplets. In fact, the 1st- and nth-order Stokes SRS intensity (at frequencies ω_{1s} and ω_{ns} , respectively) can also cause third-order sum frequency generation (TSFG) at $\omega_{TSFG} = 3\omega_{laser} - p\omega_{vib}$, where p is an integer that varies from $p = 0$ to $p = 3n$. With a Q-switched Nd:YAG laser in the near IR ($\lambda_{laser} = 1.064 \mu m$) irradiating water droplets containing polyatomic ions, the detected spectrum consists of a series of discrete peaks starting from the blue as a result of third-harmonic generation of ω_{laser} , extending to the red as a result of TSFG among the electric fields at ω_{laser} and ω_{ns} , and ending at $\omega_{TSFG} = 3\omega_{laser} - 3N\omega_{vib}$, where N is the highest-order Stokes SRS generated in the droplet. For CCl₄ droplets, the highest-order Stokes SRS can be $N = 10$. TSFG is a nonlinear optical process that has not been previously observed and identified in droplets.

The connection of these TSFG results with the main objectives of this research is as follows: We are relying on the SRS spectrum to identify the chemical composition and on the SRS intensity to infer the chemical concentration. In order not to erroneously identify all observed peaks as molecular vibration origin, it is important that we understand

other nonlinear processes which can generate frequency-shifted peaks. Furthermore, in order to deduce the concentration from the SRS intensity, it is important that we understand other nonlinear processes, such as TSFG, which can deplete the SRS intensity.

Several questions remained unanswered and we are motivated to study more in depth this four-wave mixing process in droplets. New experiments are performed on the dependence of the TSFG spectra on size of CCl_4 droplet. In addition, we measured with high-spectral resolution the TSFG spectra from H_2O droplets, when the SRS are on MDR's with different mode numbers. A considerable amount of theoretical effort is devoted to developing the following: (1) the spatial overlap of the generating nonlinear polarization and the resultant TSFG wave; (2) the frequency overlap of the generating nonlinear polarization and the resultant TSFG wave; and (3) the phase-matching mismatch between the generating nonlinear polarization and the resultant TSFG wave. A manuscript summarizing our recent results is nearly complete and will be submitted to JOSA within the next two months.

(e) Two-Photon Absorption Effects

Minority species (impurities) in liquid propellant droplets can contribute to one-photon linear absorption at the laser wavelength or frequency (λ_{laser} or ω_{laser}) and/or at the 1st-order Stokes SRS wavelength or frequency (λ_{1S} or ω_{1S}). The majority species in liquid propellant droplets can contribute to two-photon nonlinear absorption. The intensity attenuation for two-photon absorption is proportional to the square of the intensity, e.g., $I(\omega_{\text{laser}})I(\omega_{\text{laser}})$ or $I(\omega_{\text{laser}})I(\omega_{1S})$, where $I(\omega_{\text{laser}})$ and $I(\omega_{1S})$ are the intensity of the laser and of the SRS, respectively. Consequently, even if ω_{laser} and/or ω_{1S} are chosen to be in the transparent region of the liquid propellant, two-photon nonlinear absorption at frequencies corresponding to $2\omega_{\text{laser}}$ and/or $\omega_{\text{laser}} + \omega_{1S}$ cannot be avoided. Both the one-photon absorption band at ω_{1S} and the two-photon absorption band at $\omega_{\text{laser}} + \omega_{1S}$ lead to losses at ω_{1S} and, therefore, can affect the dependence of $I(\omega_{1S})$ on $I(\omega_{\text{laser}})$ and the

absolute strength of $I(\omega_{1S})$ for a constant $I(\omega_{laser})$. Since the multi-component species concentration is deduced from the absolute strength of $I(\omega_{1S})$ [for constant $I(\omega_{laser})$], it is important that we understand the role of one- and two-photon absorption (at ω_{1S}) within single droplets.

Toluene is selected as a controlled sample without either one- or two-photon absorption; m-naphthalene is selected as a controlled sample without one-photon absorption but with a well characterized two-photon absorption band in the blue wave-length region. Four discrete input laser frequencies (with $\omega_{laser1} > \omega_{laser2} > \omega_{laser3} > \omega_{laser4}$) are selected. The corresponding Stokes SRS wavelengths (with $\omega_{1S1} > \omega_{1S2} > \omega_{1S3} > \omega_{1S4}$, all in the red wavelength region) are progressively tuned out of the two-photon absorption band (in the blue wavelength region) of m-naphthalene droplets. Similar experiments are performed using toluene droplets as the controlled sample.

We are attempting to incorporate two-photon absorption effects in the standard Lorenz-Mie theory. We have encountered some minor difficulties in treating the intensity-dependent loss which in turn modifies the internal intensity distribution at the pump-laser frequency [$I(\omega_{laser})$]. Furthermore, we are attempting to model the two-photon loss each time the SRS radiation traverses the localized regions of high $I(\omega_{laser})$. We are attempting to model the following: (1) the SRS gain [proportional to $I(\omega_{laser})$] provided by the input laser intensity; (2) the two-photon loss at ω_{1S} [also proportional to $I(\omega_{laser})$] in the region of high $I(\omega_{laser})$; (3) the SRS leakage loss from the droplet [independent of $I(\omega_{1S})$] as the SRS propagates around the droplet rim; and (4) the two-photon absorption loss at ω_{1S} [proportional to $I(\omega_{1S})$], also as the SRS propagates around the droplet rim. We believe the development of a useable model that incorporates two-photon absorption loss will enable us to improve the accuracy of the multicomponent concentration deduced from the SRS intensity at the various vibrational shifts of the different species. Once we have solved the theoretical problem, we will submit a manuscript of our experimental results and theoretical model that contains two-photon absorption loss. A manuscript summarizing our

recent results on two-photon absorption effects on the SRS intensity is nearly complete and will be submitted to JOSA within the next two months.

II. CHEMICAL COMPOSITION AND SIZE DETERMINATION

(a) Nitrate Ions in Water Droplets

We measured the SRS intensity dependence on the input laser intensity $I(\omega_{\text{laser}})$.

The following four distinct regions were found: (1) the spontaneous Raman region, when $I(\omega_{\text{laser}})$ is below the SRS threshold and the output Raman intensity is linearly proportional to $I(\omega_{\text{laser}})$; (2) the stimulated Raman region, when $I(\omega_{\text{laser}})$ is above the SRS threshold and the output Raman intensity is proportional to $\exp[I(\omega_{\text{laser}})]$; (3) the saturated stimulated Raman region, when $I(\omega_{\text{laser}})$ is above the SRS threshold and the output Raman intensity is proportional to $[I(\omega_{\text{laser}})]^n$ where $n > 1$; and (4) the LIB region, when $I(\omega_{\text{laser}})$ exceeds the droplet breakdown threshold. For quantitative measuring of the species concentration within the droplet, it is important to stay within regions (2) and (3).

We also measured the SRS spectra and intensity dependence as a function of $(\text{NH}_4)\text{NO}_3$ concentration, which for liquid propellants is higher than the 8 M level we can reach in our laboratory. Once the $(\text{NH}_4)\text{NO}_3$ concentration exceeds 3 M, the SRS spectra reveal the importance of ion-ion interactions. At high molarity of nitrate ions, the spectral linewidth of the symmetric NO stretching mode significantly broadens.

We also measured the SRS spectra and $I(\omega_{\text{laser}})$ dependence as a function of the $(\text{NH}_4)\text{NO}_3$ concentration up to 4 M. For nitrate concentration up to 3 M, the $\log_e(I_{1s})$ ratio of the NO_3 mode and the water O-H mode is linear to the ratio of the concentration of the NO_3 ions and water. Above 3 M nitrate concentration, the dependence of the SRS intensity (of the NO mode) on the $(\text{NH}_4)\text{NO}_3$ concentration is no longer linear. Furthermore, beyond 4 M $(\text{NH}_4)\text{NO}_3$ the SRS signal of the O-H stretching mode becomes undetectable when $I(\omega_{\text{laser}})$ is in the $\exp[I(\omega_{\text{laser}})]$ region [region (2) mentioned above]. For liquid propellants, the concentration of the NO_3 ions exceeds 8 M. The disappearance of the SRS

of the O-H mode for concentrations exceeding 4 M is somewhat discouraging, because we originally planned to use the spacing of the SRS peaks within the spontaneous Raman linewidth of the O-H mode of water molecules to determine the droplet size.

However, the new unexpected finding is that at high molarity the spontaneous Raman linewidth of the NO_3^- mode becomes wide and the Raman gain of this mode is large enough for the SRS threshold to be reached. Once the $(\text{NH}_4)\text{NO}_3$ concentration exceeds 3 M, the $\text{NO}_3^- - \text{NO}_3^-$ interactions cause broadening of the spontaneous Raman linewidth. Furthermore, the Raman gain becomes large even at the wings of the NO_3^- symmetric stretching mode. We observed a series of SRS peaks corresponding to the MDR's located within the wings of the NO_3^- symmetric stretching mode. From the spacing of these SRS peaks, the droplet radius can be accurately deduced. We are relieved that size determination need not rely on the SRS spectrum of the O-H mode of water, which becomes undetectable for concentrations greater than 3 M, but that size determination can rely on the SRS wing spectrum of the NO_3^- mode.

We investigated the way in which the SRS intensity fluctuates with **constant** $I(\omega_{\text{laser}})$ from a single-mode laser and a multimode laser. $I(\omega_{\text{laser}})$ is determined by measuring the energy of the laser pulse and dividing by the halfwidth of the pulse duration and the area of the focal spot. The temporal profile of the single-mode laser pulse is smooth, while that of the multimode laser pulse consists of numerous spikes. Results from ≈ 700 laser shots [at constant $I(\omega_{\text{laser}})$] are plotted in a histogram form. Two features are noteworthy. First, the average SRS intensity is higher with multimode laser input. Second, the SRS intensity fluctuation is much larger with multimode laser input. Our results clearly indicate that, in order to use the SRS intensity as a quantitative measure of the NO_3^- concentration, it is essential that a single-mode laser be used.

In order to bridge the gap between single droplet studies and spray, which is usually produced by a high pressure injector, we conducted a study of SRS from a spray produced by an oil burner nozzle (hollow cone type). Three results are noteworthy.

(1) Only the larger size droplets exhibited SRS while all droplets, liquid ligaments, and vapor caused intense elastic Lorenz-Mie scattering. (2) The SRS peaks associated with the nitrates and the O-H stretch mode of water are readily observable for 3 M $(\text{NH}_4)\text{NO}_3$ water droplets. (3) The ratio of the natural logarithm of the nitrate SRS is linearly proportional to the concentration only within a certain narrow input intensity range, where $I(\omega_{1s})$ is proportional to $\exp(\omega_{\text{laser}})$.

Based on our spray results, it is apparent that larger size droplets have a lower SRS threshold, while droplets of all sizes give rise to intense elastic (Mie) scattering. Furthermore, in order to bridge the gap between the results from single droplets in air with those from droplets which are approaching the critical condition, we considered the Q factor of the MDR's as the ratio of the index of refraction of the liquid and the surrounding approaches 1. Assuming that a minimum Q factor of 10^6 is needed for SRS, we now know the lower limit of droplet radius and ratio of index of refraction. In addition, we also know how the density of MDR (i.e., the number of droplet cavity modes per 10 cm^{-1}) decreases as ratio of the index of refraction of the liquid and surrounding approaches 1. For details of the SRS studies with nitrate ions, see publication 6.

PUBLICATIONS RESULTING FROM THE RESEARCH

Fundamentals of Nonlinear Optical Effects

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2. R.K. Chang, D.H. Leach, and J.-Z. Zhang, "The Q factor of Micrometer-Size Droplets as Optical Cavities," in Proceedings of the U.S.-Mexico Workshop on Electrodynamics of Interfaces and Composite Systems, Taxco, Mexico, August 10-14, 1987, R.G. Barrera and W.L. Mochan, eds. (World Scientific Publishing Co., 1988), p. 373.
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Composition and Size Determination

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